

The University of Chicago

THE MAXIMUM
BUBBLE PRESSURE METHOD FOR
THE MEASUREMENT OF
SURFACE TENSION

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1934

By
HARLEY PRICE TRIPP

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1940

The University of Chicago

THE MAXIMUM
BUBBLE PRESSURE METHOD FOR
THE MEASUREMENT OF
SURFACE TENSION

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1934

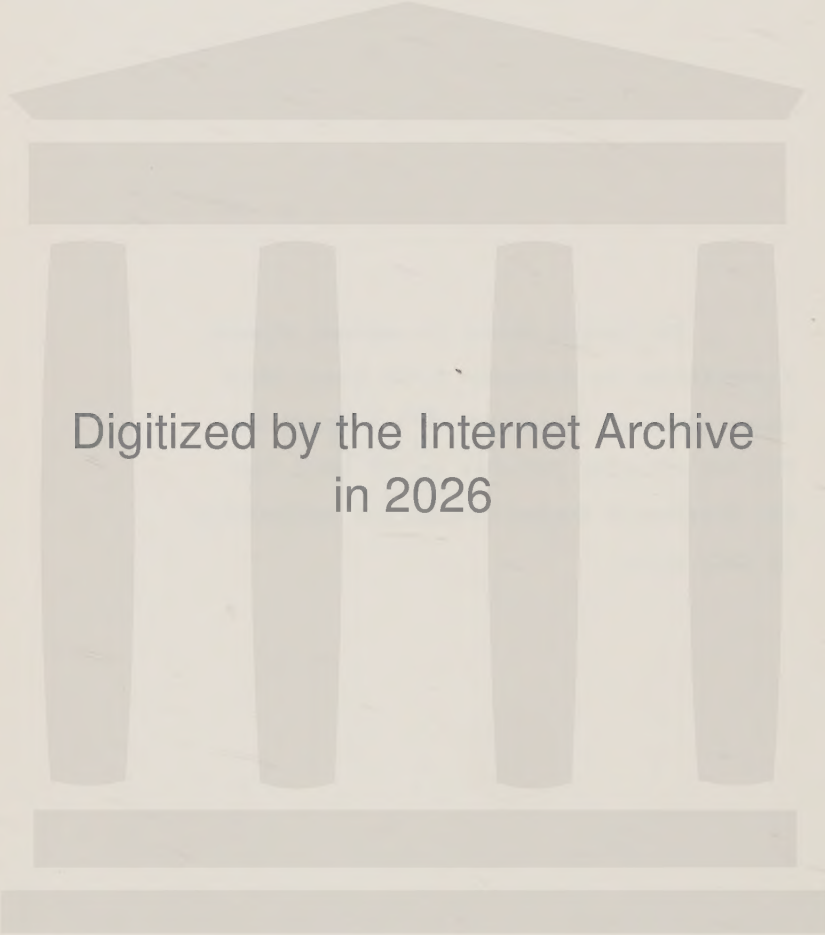
By
HARLEY PRICE TRIPP

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1940



The author wishes to express sincere appreciation to Professor T. F. Young under whose guidance this research was conducted, for his untiring interest in the work, and his invaluable suggestions in the preparation of this paper.



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41533925_0073

INTRODUCTION

There are four methods which are commonly used for the measurement of surface tension. These involve respectively: the rise of a liquid in a capillary tube, the weight of a drop, the maximum pull required to lift a ring through the surface of a liquid, and the maximum pressure attained in the liberation of a bubble. The first three of these have often yielded incorrect results partly because of poor technique but principally because of incorrect interpretations of fundamental principles. Recent careful studies of these three methods have shown that errors have amounted to as much as three per cent in the capillary height^{1,2} method, and to more than 40% in the drop weight³ and ring methods.⁴ The maximum bubble pressure method, although it has been extensively used by Jaeger⁵ and by Sugden,⁶ has not yet been thoroughly investigated. Many of the results of Sugden seem to be approximately correct, but the numerous data of Jaeger are seriously in error.

The purpose of this paper is to investigate the fundamental theory of the maximum pressure in bubbles and the practical application to surface tension measurements.

¹Richards and Coombs, J. Am. Chem. Soc., 37, 1656-76 (1916).

²Harkins and Brown, J. Am. Chem. Soc., 38, 246 (1916).

³Harkins and Humpéry, J. Am. Chem. Soc., 38, 228 (1916).

⁴Harkins, Young and Cheng, Science, 64, 333 (1926).

⁵Jaeger, Zeits. Anorg. Chem., 101, 1 (1917).

⁶Sugden, J. Chem. Soc. (London), 121, 858 (1922).

Simon,¹ who first suggested the method, assumed that the maximum pressure incurred in the liberation of a bubble in any liquid is equal to the pressure necessary to depress a meniscus by an amount equal to the capillary rise. This is true only for tubes of infinitesimal radius. Cantor² gave the first correct theory of the formation of bubbles from tubes of finite radii, but deduced the following incorrect equations for the manometric pressure—in which the symbols have the meaning shown in Table I:

$$\gamma = \frac{\bar{p}r}{2} \left[1 - \frac{2}{3} \frac{r}{h} - \frac{1}{3} \frac{r^2}{h^2} \dots \right]$$

TABLE I

Symbols Used Most Frequently

r	= radius of the tip
γ	= surface tension in dynes per centimeter
D	= density of the liquid
d	= density of the light phase
g	= the acceleration of gravity
$\bar{p}$	= the maximum pressure difference inside and outside the bubble at the level of the end of the tip
$h = \frac{\bar{p}}{(D - d)g}$	
p	= the pressure difference at varying depths on the two sides of a bubble
a	= the square root of the capillary constant
b	= the radius of curvature at the vertex of a bubble or meniscus
j	= the height of the vertex of the bubble above the tip of the tube
P_0	= the pressure difference between the two sides of any bubble or meniscus at the vertex

¹Simon, Ann. Chim. Phys., 33 (1851).

²Cantor, Weid. Ann., 47, 399 (1892).

Later Cantor¹ deduced another equation which likewise is incorrect:

$$\gamma = \frac{\bar{p}r}{2} [1 - \frac{2}{3} \frac{r}{h} - \frac{1}{2} \frac{r^2}{h^2} \dots]$$

Feustel² gave an incorrect expression:

$$\gamma = \frac{\bar{p}r}{2} [1 - \frac{2}{3} \frac{r}{h} - \frac{r^2}{h^2} \dots]$$

Ferguson³ gave the equation:

$$\gamma = \frac{\bar{p}r}{2} [1 - \frac{2}{3} \frac{r}{h} - \frac{1}{\sqrt{6}} \frac{r^2}{h^2} \dots]$$

which Schrodinger⁴ and later Verschaffelt⁵ have concluded to be in error. Schrodinger gave the formula:

$$\gamma = \frac{\bar{p}r}{2} [1 - \frac{2}{3} \frac{r}{h} - \frac{1}{6} \frac{r^2}{h^2} \dots] \quad (1)$$

which Verschaffelt has confirmed.

Sugden has shown that this equation, derived for small values of r/a , is in accord with the Tables of Bashforth and Adams for $r/a = .2$. To facilitate calculations he has defined a quantity X by the equation

$$X = \frac{a^2}{h_m}$$

in which h_m is the maximum value of h attained in the liberation of a bubble. He has prepared a table of values of $\frac{X}{r}$ corresponding to values of r/a from 0 to 1.5. For his calculations of $\frac{X}{r}$ between $r/a = 0$ and $.2$ he used the Schrodinger Equation in the following form:

$$\frac{X}{r} = [1 - \frac{2}{3} \frac{r}{h} - \frac{1}{6} \frac{r^2}{h^2} \dots].$$

¹Cantor, Ann. Physik, 7, 698 (1902).

²Feustel, Ann. Physik, 16, 61 (1905).

³Ferguson, Phil. Mag., 28, 128 (1914).

⁴Schrodinger, Ann. Physik., 46, 413 (1915).

⁵Verschaffelt, K Akad. Amserdam Proc., 21, 365 (1912).

His table was completed by substitution of values from Bachforth and Adams' Tables in the equation

$$\frac{X}{r} = \left[\frac{X}{b} + \frac{z}{b} \cdot \frac{r\sqrt{b}}{a|z} \right].$$

These calculations yield the difference between the pressure within the bubble and that in the liquid phase at the level of the tip. The experimentally measured pressure must be corrected for the hydrostatic pressure due to the depth of immersion of the tip below the surface. This can be done if the apparatus is constructed with an auxiliary well of liquid, as represented by the dash lines in Figure 1. Apparatus of this design has not hitherto been used. Sugden eliminated the correction for this immersion by the use of two capillary tubes of different radii immersed to the same depth. He measured the pressure necessary to liberate bubbles from each, and from the difference calculated the surface tension by the use of the equation

$$a^2 = \frac{(h_{m1} - h_{m2})}{(1/X_1 - 1/X_2)}.$$

The pressures, h_{m1} and h_{m2} , are related to X_1 and X_2 by the equations

$$h_{m1} = \frac{a^2}{X_1} + t \text{ and } h_{m2} = \frac{a^2}{X_2} + t,$$

in which t is depth of immersion of the tip. If the radii of the tip r_1 and r_2 are known, a^2 may be determined with the aid of Sugden's Table of minimum values of $\frac{X}{r}$.

Frese¹ and Hoffman² working in this laboratory have shown that the mathematical theory is in accordance with experiment if the bubbles are formed slowly. Slow bubbling has been used by a

¹Unpublished work.

²Masters Thesis, University of Chicago, 1926.

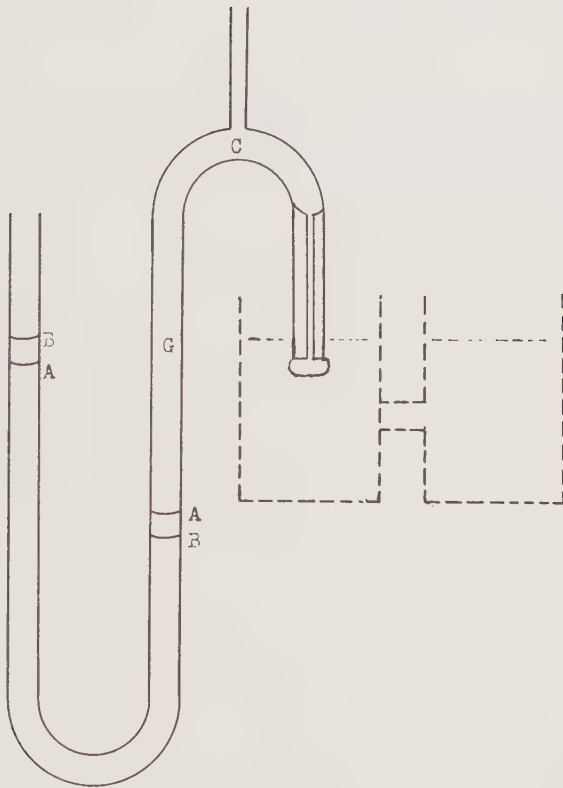


Figure 1

number of investigators. Bubbles from Sugden's small tubes, however, were not formed slowly but at the rate of about one per second. He did not state how the observed pressures compare with those obtained when a maximum pressure is approached gradually.

He writes:

Bubbles soon commence to issue from the capillary tube and the rate of flow in the aspirator is then adjusted until single bubbles are formed at the rate of about one per second. A slight oscillation of the gauge will be noted as each bubble is detached, and the maximum pressure recorded by the gauge is noted.¹

His results are often higher than those obtained by other methods. It is possible that the good agreement in some cases is due to accidental compensation of errors. The phenomena are very complex when bubbles are formed rapidly. For example, if the liquid is lowered below the tip of the capillary while bubbles are emerging at the rate of one per second the friction in the tube may under certain circumstances maintain a pressure as high as 30% of the original.

It is the purpose of this investigation to extend the work of Frese and Hoffman and to investigate the effect of the rate of bubbling upon the maximum pressure.

¹Sugden, The Parachor and Valency, p. 210. New York: Alfred Knopf, 1930.

HISTORY OF THE BUBBLE

Shape of Bubble Formed on Capillary: Before discussing the theory of the maximum bubble pressure method let us trace the history of a single bubble formed on the tip of a capillary tube with walls of infinite thickness. If the angle of contact which the liquid surface makes with the tip is zero, its growth is illustrated by the solid lines of the left hand portion of Figure 2, which represents various sizes and shapes of the bubble as it expands. For this discussion it is convenient to treat the development of the bubble in three stages:

1. The downward displacement of the meniscus in the capillary tube until its upper edge reaches the tip. During this period the shape of the meniscus remains constant.

2. The expansion of the bubble from the meniscus stage (curve b) until its surface at the line of contact has become tangent to the horizontal surface of the tip (curve d). The angle lying between the vertical and the normal to the surface at the line of contact, which we designate by ϕ' remains constant during the depression of the meniscus in the tube (first stage), but changes during the expansion (second stage) from 90° to 180° . See Figure 3.

3. The further expansion of the bubble with $\phi' = 180^\circ$. During this stage the circle of contact r_0 of the bubble with the horizontal edge of the tip increases indefinitely, and consequently the shape now bears no relation to the radius of the tip.

Shape of Bubble Formed under Plate: Figure 4 represents a plate so placed that the edge of its conical perforation lies

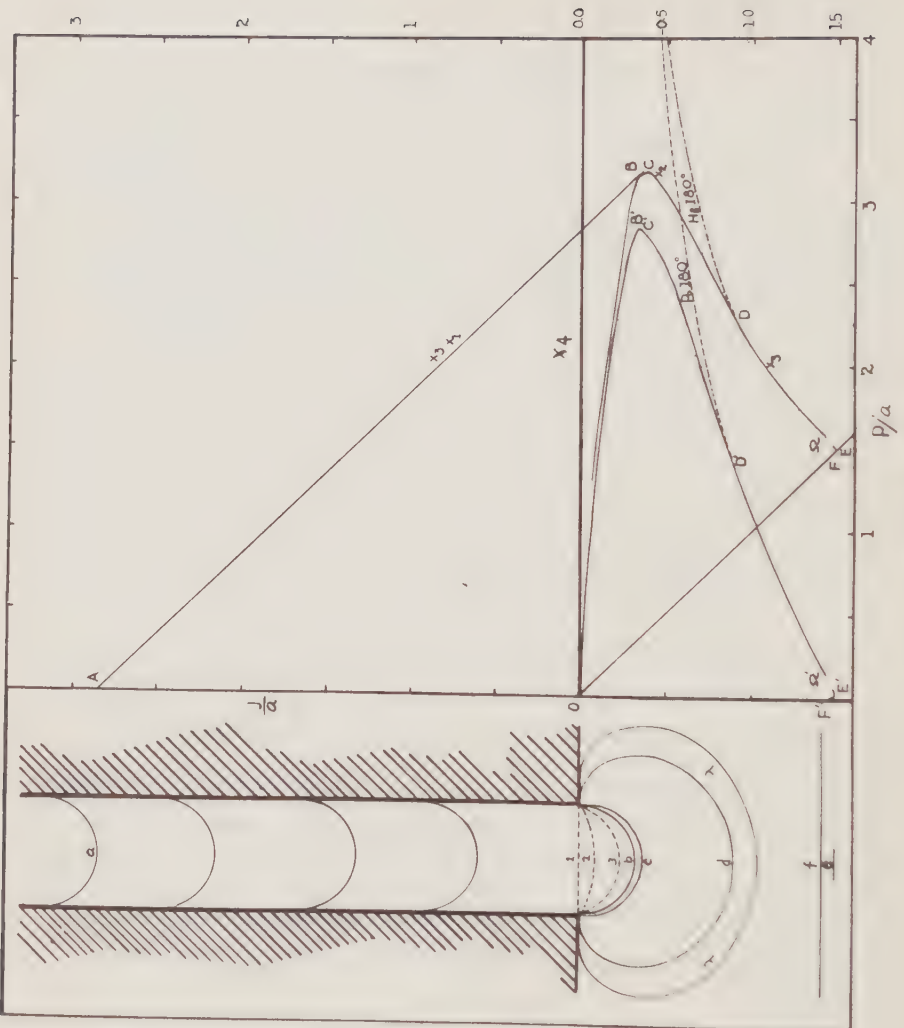


Fig 2

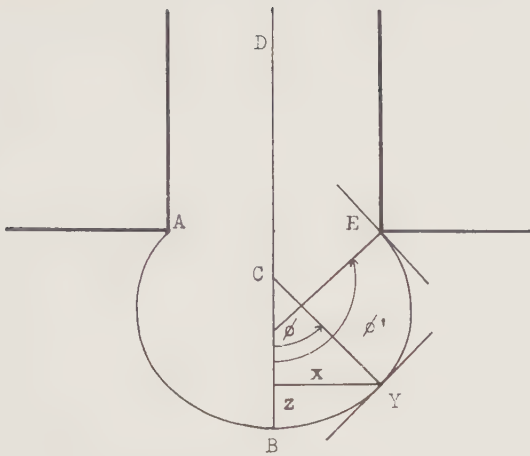


Figure 3

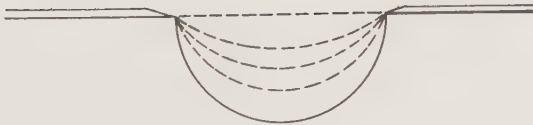


Figure 4

in the surface of the liquid.¹ If pressure be applied to the free surface of the liquid it is depressed and passes through a series of shapes represented by the dashed lines on Figures 2 and 4. The straight dash line represents the surface when the applied pressure is zero. Under this condition ϕ' is zero. The other lines of Figure 4 represent in turn shapes of the meniscii as the pressure is increased. The last curve on this figure corresponds to a meniscus whose ϕ' is 90° . When more gas is forced into the

¹In this discussion the thick plate with conical perforation is preferred to the infinitesimally thin plate which is not experimentally obtainable. The argument is the same for both.

bubble it expands beyond the ninety degree form. The larger bubbles are identical with those formed on a tube and are represented, therefore, by the solid line in Figure 2.

Pressure: On Figure 2 the pressure in the bubble (abscissa) is plotted as a function of j , the height of the vertex above the tip as (ordinate). The tip is assumed to be placed in the free surface since this position is most convenient for our purpose. Curve AB represents the pressure necessary to depress the meniscus to the various positions within the capillary. This pressure is zero when the meniscus is at its normal height, and is proportional to the displacement from that position. If the pressure is measured in a manometer containing the same liquid as that in which the bubble is formed the pressure is equal to the displacement. Thus a depression of x centimeters in the capillary requires a pressure which causes a difference in height of x centimeters in the two arms of the manometer. Because of the simplicity of this and similar relationships, we shall in general express pressures in terms of the reading of such a manometer.

Let P_0 represent the pressure difference between the two sides of any bubble or meniscus at its vertex. Curve OB'F' represents P_0 of a meniscus formed under a perforated plate of infinitesimal thickness. The sections OB', B'D', and D'F' represent respectively the pressure as ϕ' increases from 0° to 90° , from 90° to 180° and the further expansion of the bubble. Since a bubble formed below a plate and one formed on the tip of a tube are identical when ϕ' is equal to or greater than 90° , the curve between B'F' represents the pressure difference between the inside and outside of a bubble below either a plate or a tube. The point B' represents the maximum value of the pressure difference for either type of a bubble.

The line OF represents the difference in the pressure at the free surface of the liquid and in a horizontal plane within the liquid at the height of the vertex. The symbol j which represents the height of the vertex above the origin is therefore, the negative of the pressure. Line OF consequently has a slope of minus one (i.e., 45°).

Curve OBF represents the pressure inside the bubble minus that in the free surface. Obviously, this is the sum of the pressures P_0 (curve OB'F') and j (line OF). The whole curve applies to a bubble under a plate. That section of it between B' and F' is also applicable to a bubble formed on a capillary tube.

The pressure change throughout the history of a bubble formed on a capillary tube can be traced on the curve ABF. The portion AB represents the depression of the meniscus in the tube. When the upper edge of the meniscus reaches the tip of the tube the pressure has the value at B. The shape is now represented by curve b, Figure 2. As more gas is forced in and the vertex is depressed further, the pressure rises less rapidly than hitherto. When the bubble attains the shape c the pressure has reached a maximum value shown at C. As more gas is forced in, the expansion is so rapid that the pressure decreases. During this expansion ϕ' increases further and the bubble attains shape d when ϕ' reaches 180° . The pressure is now shown at D. When more gas is added ϕ' can no longer increase because of the horizontal surface of the tip. The circular line of contact now begins to increase, and the pressure follows the course DEF. Point F represents the pressure and depth of a bubble of infinite volume. The curvature at the vertex of such a bubble is zero and the pressure is therefore due solely to j . F is therefore on the line having the slope of minus one. According to an equation of Verschaffelt which is

to be discussed later, the depth of the bubble passes through a maximum at point E. The radius of curvature of this bubble of maximum depth can not be zero and the pressure in such a bubble must be greater than j . The point E therefore lies to the right of OF.

During the third stage when $\phi' = 180^\circ$, the forms of all bubbles having a given circle of contact will be identical and the pressure will likewise be the same. The curve DF therefore is representative of any bubble whose circle of contact is greater than the bore of the tube.

The maximum pressure (point C) occurs when $\frac{dHg}{dj}$ is zero as was pointed out in Hoffman's Thesis. This point is reached when

$$\frac{dP_o}{dj} = \frac{dj}{dj} = 1$$

in other words: the slope of OB'F' is unity as at C'.

Computations: The diagram (Figure 2) has been constructed with precision in order to correlate and explain experimental data discussed below. The data will be necessary for comparison with experiment and for further argument. They are not at present of interest. Only the methods of calculations are described herewith; the tables are in the appendix.

In Figure 3 let ABE be the outline of a bubble emerging from a capillary tube. Define any point Y on the surface by the coordinates x and z referred to the tangent and normal at B as axes. Let ϕ define the angle lying between the normal at Y and the axis BD.

The general La Place Equation of a free surface is

$$\frac{1}{R} + \frac{1}{R'} = \frac{p}{\gamma} \quad (2)$$

in which R and R' are the principal radii of the curvature of the surface at any point y , and

$$p = g(D - d)z + \text{Constant.} \quad (3)$$

The section YC which lies between Y and the axis z is one of the radii of curvature of the plane curve ABE, i.e., a meridional section. Then,

$$\left(\frac{1}{\rho} + \frac{\sin \phi}{x}\right) = g(D - d)z + \text{Constant} \quad (4)$$

Let b represent the value of $\frac{x}{\sin \phi}$ and the limit of $\frac{x}{\sin \phi}$ at the origin; then $z = 0$, and the

$$\text{Constant} = \frac{2\gamma}{b}. \quad (5)$$

Equation (3) may now be written

$$p = g(D - d)z + \frac{2\gamma}{b}. \quad (6)$$

Then

$$\left(\frac{1}{\rho} + \frac{\sin \phi}{x}\right) = \frac{2}{b} + z(D - d)g. \quad (7)$$

Multiply through by $\frac{b}{\gamma}$:

$$\left(\frac{b}{\rho} + \frac{\sin \phi}{x/b}\right) = 2 + \frac{(D - d)gbz}{\gamma} \quad (8)$$

β is commonly defined by

$$\beta = \frac{2b^2}{a^2}$$

Then

$$\left(\frac{1}{\rho/b} + \frac{\sin \phi}{x}\right) = 2 + \frac{z}{b} \quad (9)$$

In the equation above $\sin \phi$ can be expressed in terms of the first and second differential coefficients of z with respect to x and equation (9) may be written

$$\frac{d^2 z'}{dx'^2} + 1 + \frac{(dz')^2}{(dx')^2} \frac{dz'}{x'dx'} = (2 + z) \frac{1}{b} + \frac{(dx')^2}{(dz')^2}^{3/2} \quad (10)$$

This is a differential equation of the second order which cannot be directly integrated. Each value of β represents a member of a family of curved surfaces as those shown in Figure 2. By suitable mathematical methods, the coordinates of these curves may be determined with any desired degree of accuracy. For many

values of β Bashforth and Adams give the coordinates of the respective surfaces tabulating z/b and x/b for various values of ϕ from 0° to 180° .

Their calculations required many years and help of collaborators. They are complete for the values of $b = .125$ to 100 . Large values of β , corresponding to very large bubbles, are not included in their tables. It is therefore necessary to use approximate equations for the treatment of the larger bubbles.

The construction of the curves in Figure 2, which represent the shape of the meniscus or bubble, may be explained by an example. The figure was constructed to represent the phenomena occurring in water at 25° . When the radius of the capillary is $.1300$ cm.—a value encountered in the experimental work of Frese, r/a was, therefore $.3386$. For the bubble whose $\phi' = 90^\circ$ and whose $r/a = .3386$, we shall determine the value of z/b for $\phi = \phi' = 90^\circ$, and the values of x/a and z/a for $\phi = 30^\circ$.

It is necessary to determine by interpolation in Bashforth and Adams' Tables and successive approximation, the appropriate value of the parameter β from the equation

$$\frac{r}{b} = \frac{x}{b} = \frac{r\sqrt{2}}{a\beta} \quad (11)$$

This condition is satisfied when $\beta = .2470$. When $\phi = 90^\circ$ and $\beta = .2470$, $\frac{z}{b} = .9174$, $\frac{x}{b} = .9634$, and $\frac{b}{a} = .13493$.

Hence $\frac{x}{a} = .3386$ and $\frac{z}{a} = .3224$.

For $\phi' = 30^\circ$ and $\beta = .2470$ the values of x/b and z/b were found by interpolation to be respectively: $.4958$, and $.1308$ —from which we find $x/a = .1743$ and $z/a = .04651$. When $\phi = 90^\circ$, x/a is r/a , which $= .3386$ and z/a , which is j/a ($1/a$ times the height of the bubble above the tip) is $.3224$.

The coordinates of the curves a to d were determined for

convenient values of ρ and are tabulated in the appendix tables. Since the curve λ was not required to conform to any particular value of r/a , a value of $\beta = 2$, was arbitrarily selected for convenience of calculation.

To use the Bashforth and Adams' Tables for the determination of the pressure, we divide equation (6) by $g(D - d)$, then

$$\frac{p}{g(D - d)} = z + \frac{2\gamma}{g(D - d)} \cdot \frac{1}{b} \quad (12)$$

The capillary constant is

$$a^2 = \frac{2\gamma}{g(D - d)}$$

and (12) becomes

$$\frac{p}{g(D - d)} = z + \frac{a^2}{b} \cdot \quad (13)$$

To find the pressure in centimeters of the liquid itself we have

$$Hg = h = z + \frac{a^2}{b} \quad (14)$$

for the final pressure, since

$$p = h(D - d)g.$$

For our problem $z = j$; then

$$Hg = j + \frac{a^2}{b} \cdot \quad (15)$$

But P_0 , the pressure difference between the inside and the outside of the meniscus or bubble, may be determined by adding the pressure j to Hg . Thus,

$$P_0 = j + \frac{a^2}{b} - j = \frac{a^2}{b} \quad (16)$$

OB'F' was determined from equation (16). The few values of $\frac{a}{b}$ calculated for the curves and bcd were substituted in the equation. Other values of P_0 on the curve between O and Ω' were determined from β arbitrarily selected for convenience. The values of r/a and j/a , were calculated for the same values of β . Between O and D it seemed most convenient to choose a value of ρ'

and to interpolate for the corresponding value of β . From D to it was much more convenient to select a rounded value of β since β' was necessarily 180° .

The portion of the curve $\Omega' F'$ is outside the region of Bashforth and Adams' Tables, and it was necessary to use other approximate equations for the calculation of b . There are a number of equations relating j/a , b/a and L/a , where L is the maximum radius of the bubble. A criticism of these equations constitutes no part of this discussion; we are concerned with them merely for the construction of the illustrative curves and we shall accept the pair of equations given by Verschaffelt.¹ The results given by his equations agree approximately with the curves extrapolated from the calculations of Bashforth and Adams. They are not far from correct and are satisfactory for our purpose.

Verschaffelt's equations may be written in terms of our symbols, thus

$$\frac{a}{b} = 1.94 \sqrt{\frac{L}{a}} e^{-\sqrt{2} \frac{L}{a}} \quad (17)$$

and

$$\frac{1}{a} = \frac{a}{3L} - \frac{a}{b} + \sqrt{2} \quad (18)$$

Equation 17 was used to determine the values of $\frac{a}{b}$ for large bubbles which have a maximum radii L , equal to 3, 4, 5, and 6. P_0 was then calculated by the substitution of these values of $\frac{a}{b}$ into equation 16. The values of $\frac{1}{a}$ were determined from equation (18).

Curve OCF which is the sum of j and P_0 was computed from the values of j/a and P_0 which have just been discussed. The construction of curves OF and AB have been discussed in a previous

¹Verschaffelt, K. Akad. Amsterdam Proc., 21, 836, 1919.

section in which it was shown that their slopes are a minus one.

Calculations for other Values of r/a : In Figure 5 are curves corresponding to the values of $r/a = .3081, .3386, .4021,$ and 1. Curve 1 corresponds to the dimensions of the tube used in this study. Curve 2 and 3 were calculated for tubes used by Frese. Curve 4, which was constructed for illustration, was calculated in part from values given by Sugden.

For infinitely large values of r/a , the radius of curvature at the vertex of the bubble is infinite and the maximum pressure is equal to the difference in pressure between the free surface and the vertex of the bubble. Under these conditions Curve ABF is reduced to line OF. The maximum pressure is given by the relation

$$\frac{1}{a} = \sqrt{2}.$$

As the value of r/a decreases, the pressures corresponding to the same depths of the bubble are greater. The slope of the section of the curve CD approaches zero as the ordinate approaches zero.

The three points B ($\phi' = 90^\circ$), C (maximum pressure), and D ($\phi' = 180^\circ$) are characteristic of the given value of r/a and represent significant points in the behavior of the bubble. The pressure and depth corresponding to $\phi' = 90^\circ$ vary. They are represented for a continuous series of the value of the parameter r/a by the curve B. Curve C shows a similar variation of the maximum pressure and the curve D of the pressure and depth when ϕ' becomes 180° .

The significance and course of curve D has been discussed. It is representative of all bubbles whose radius of contact is greater than the radius of the bore. Curve C, Figure 2, which represents the variation of the maximum pressure terminates at

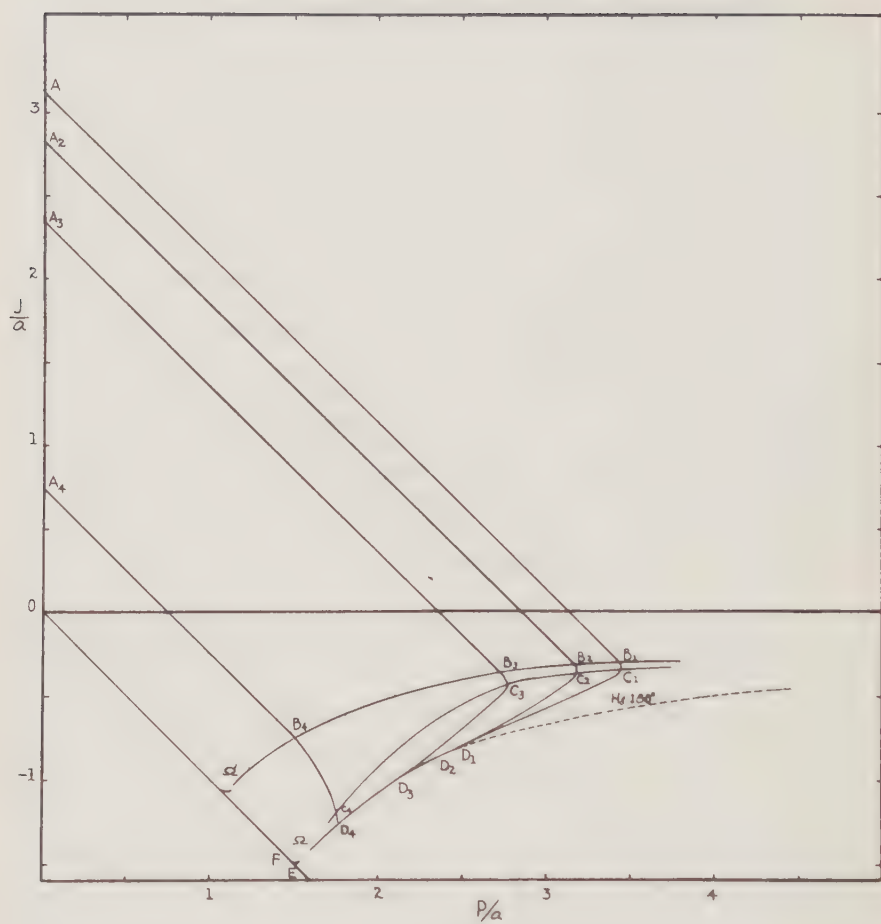


Fig. 5

point F which represents the limit of the height and pressure approached as the bubble increases to an infinite diameter. For small values of r/a this curve approaches curve B. In the region where there is no appreciable difference between these curves, the simple equation

$$\gamma = \frac{r}{2} \{H_{gm} - gd(r + t)\}$$

relates γ and H_{gm} the maximum pressure. Over the range in which this equation is valid the bubble may, until it has reached the maximum pressure, be considered a hemisphere. It is not practical to use tubes of the radii which correspond to this region of the plot to make absolute measurements because of the difficulty encountered in the determination of the diameters of small tubes. When larger tubes are used so that the radius may be determined with small percentage error, the simple equation is not valid. The methods dealing with larger values of r/a have been discussed.

The calculation of the points on curve D and the solid portion of curve B has been discussed in the previous section. The values of j for the dash portion of curve B has been determined from an equation given by Verschaffelt.

$$\frac{1}{a} = \sqrt{.6096 \frac{a}{b} - \frac{2j}{b} + 1} \quad (19)$$

where the values of $\frac{a}{b}$ were calculated from equation 17. The pressures were calculated by the relation

$$\frac{H_g}{a} = \frac{a}{b} + \frac{1}{a}$$

The data for the respective curves are found in Tables 2, 8, 9, and 13.

Experimental Confirmation of Curve CE: Frese confirmed experimentally the portion of the curve ABD (Figure 2) in the region of the maximum pressure. That portion of the curve between

C and E which lies in the region of D was confirmed in this study.

The apparatus used is similar to that shown in Figure 1. The tip, made from a piece of capillary tubing was ground to a smooth surface perpendicular to the walls. The diameter, determined from the average of ten or more successive measurements at each of three points approximately 60° apart, was .2366 cm. The calculated maximum pressure H_{gm} for water is 1.3267 cm. The pressure generator consisted of a small vice and five centimeters of rubber hose with an inside diameter of .4 cm. The screw of the vice had been replaced by one with 80 threads to the inch. The diameter of the gauge was about .4 cm. The diameters of the two wells of the container were 4.3 cm and 1.7 cm. The total volume of the system (which varied for each point) ranged from 60 to 90 cm^3 . The density of the gauge liquid determined with an Ostwald modified pyknometer was .9626. The average depth of immersion of the tip below the surface of the liquid in the side arm was .554 cm. No allowance was made for the rise of the liquid in the container as the bubble increases in size. The value of this correction, less than .0005 cm, could not be determined with the cathatometer.

These measurements were made incidentally while studying the influence of a variable volume upon the behavior of the system. A description of the procedure will be given in a later section. The experimental data are given in Table II. The experimental height of the bubble j in centimeters is given in the first column. In the second and third column are given the corresponding experimental and theoretical pressures in centimeters of water. In the fourth column is given the difference in pressure between the experimental and the theoretical values. This essentially constant difference, .503 cm, represents the depth of the tip

below the free surface of the liquid. This value may be determined directly from measurements made at the maximum pressure. The calculated pressure necessary to liberate bubbles when the tip is in the free surface of the liquid is 1.327 cm. In the experiment the maximum applied pressure was 1.828 cm. The difference .501 cm is within experimental error of that found above, namely, .503 cm. The largest deviation from the mean value .503 found in column 4 represents .3% of the applied pressure. In a surface tension measurement where this tube would be used in conjunction with a smaller one (.01 cm radius) this error would be less than .02%. In the last column are given the experimental data corrected by the average deviation from the theoretical curve. Thus there is excellent agreement between the theoretical and experimental curves.

TABLE II
Theoretical and Experimental Values of H_g
and j for a Bubble Formed in Water

j	H_g Experimental uncorrected for depth of immersion	H_g Theoretical	ΔH_g	H_g Experimental corrected by average deviation from theo.
.361	1.355	.851	.504	.852
.352	1.374	.870	.504	.871
.335	1.413	.907	.506	.910
.314	1.446	.948	.498	.953
.309	1.465	.961	.504	.962
.300	1.483	.980	.503	.980

THE FREE EXPANSION

An apparatus of the general form shown in Figure 1 except for the well represented by the dash lines is commonly used to measure surface tension by the maximum bubble pressure method. The process consists of the forcing of gas into the apparatus and the measurement of the maximum pressure necessary to liberate bubbles.

Once the maximum pressure has been attained in the formation of a bubble, the subsequent decrease in pressure as represented by curve CF (Figure 2) cannot influence the maximum pressure attained in that particular bubble but it may affect the determination of the maximum pressure of the following bubble. Obviously, if sufficient time is allowed to elapse before the formation of a second bubble there will be no influence of one bubble on the next. However, when the interval of time is short, as in the method used by Sugden, friction and inertia may materially affect the pressure in the succeeding bubble.

To study the growth of the bubble, advantage has been taken of a technique developed by Frese. Using a relatively large tube he was able to retain the bubble on the tip and pass varying amounts of gas into it. Confirming ABD (Figure 2), he found that under certain conditions he was able to determine the height and pressure up to or a little beyond the maximum pressure. When he attempted to continue the curve beyond point C the system became unstable and the expansion of the bubble could not be controlled. He found that decreasing the diameter of the gauge made it possible to control the bubble over that region.

When his gauge was sufficiently small he was able to determine all of the portion of the curve in which he was interested, namely, that section in the neighborhood of the maximum pressure. These points which he was able to determine with the large gauge agreed exactly with the curve determined with a very small gauge. In other words, all the points whether determined with a large or small gauge fit smoothly on the same curve—a curve later verified mathematically by Hoffman. The large gauge merely prevented the retention and measurement of the bubble between certain depths.

The phenomena associated with these uncontrolled expansions seemed likely to prove very interesting; investigation has revealed that they are important in certain applications of the bubble pressure method to surface tension measurements. When the dimensions of the apparatus are such that a part of the expansion cannot be controlled, the growth of the bubble may be considered in two parts. The first, which will be called the reversible expansion, includes the behavior of the bubble during the time it is necessary to force gas into the system to cause the expansion. This process is reversible and the height of the bubble and the pressure may be determined at any time. The second, which will be called the free expansion, may or may not start at the time the pressure in the system is at a maximum. It is characterized by a continued expansion of the bubble, and further decrease in pressure indicated by the gauge.

Both the volume of the gas space and the cross-section of the gauge have been shown to be important factors in the production of the uncontrolled expansion. The volume of the gas space includes tube G (Figure 1), the connecting tube C, the capillary tip b, the bubble, and the pressure generator. The total volume V_t , when the applied pressure is zero will be designated by V_0 ,

then

$$V_t = V_o + V_g + V_b + V_c. \quad (20)$$

where V_g represents the volume of the liquid displaced due to the motion of the gauge, in which V_o represents the increment of volume of the pressure generator, and V_b represents the increment of volume produced by the depression of the meniscus in the capillary tube.

The volume change V_g which is due to the motion of the liquid in the manometer may be calculated as a function of the pressure change by the relation

$$(V_{g2} - V_{g1}) = (P_2 - P_1) \frac{A}{2}$$

where $(P_2 - P_1)$ is the distance through which the gauge fluid moves (AB, Figure 1), and A is the cross-section of the gauge. When the liquid used in the gauge is not the same as that in which the bubble is formed, the quantity of gas displaced by the motion of the gauge fluid is larger or smaller by an amount determined by the ratio of the densities of the liquid. If s is the density of the liquid used in the gauge and D that of the liquid in which the bubble is formed, A of the equation above must be replaced by

$$A' = \frac{D}{s} A,$$

thus

$$(V_{g2} - V_{g1}) = (P_2 - P_1) \frac{A'}{2} \quad (21)$$

The change of the total volume may be expressed in terms of the pressure P_2 and the initial pressure P_1 .

$$V_{t2} - V_t = (P_2 - P_1) \frac{V_o}{P_2}$$

Since the change in pressure P in the experiments to be described is always small (never greater than .2%) the approximate equation

$$(V_{t2} - V_t) = (P_2 - P_1) \frac{V_o}{P_1} \quad (22)$$

may be substituted for equation (21) whenever it is more convenient.

The volume change ($V_{b2} - V_{b1}$), as long as the upper edge of the meniscus remains inside the capillary, is related to the pressure by the following relation

$$(V_{b2} - V_{b1}) = (P_2 - P_1)(w) \quad (23)$$

where w is the cross-section of the bore of the tip. After this position is passed the volume is determined by the relation

$$V_b = (V/b^3)b^3 + V_d.$$

The ratio of V , the volume of the bubble proper, to b^3 may be taken from Bashforth and Adams' Tables. The quantity V_d is the volume of liquid in the capillary when the meniscus is in its normal position. It is equal to the product of the cross-section of the capillary and the average height of the meniscus; thus,

$$V_d = (r^2) (h_{av}) (3.14) = ra^2 \cdot 3.14$$

$$V_b = (V/b^3)b^3 + ra^2(3.14) \quad (23a)$$

The volume represented by V_t , V_g , V_b and $V_g + V_t$ for a series of pressures are given in Table 16. A set of conditions for one experimental case were: the atmospheric pressure was 74 cm of mercury or 1006.4 cm of water. This was P_1 . V_0 was 3.5 cm³. The radius of the tip was .1183 cm. The capillary constant for water is .14743 cm²; hence a is equal to .38399 cm, and $r/a = .3081$. The average cross-section of the gauge was .1192 cm². This value was determined from the change in the level of the arms of the gauge produced by the withdrawal of a quantity of water. A' was then calculated from the value of the cross-section, the density of water, .9970 at 25°, and the density of the gauge liquid, .9626.

$$A' = \frac{.9970}{.9626} (.1192) = .1234 \text{ cm}^2.$$

The calculation of V_t , V_g , and V_b may be illustrated as follows. When $P_2 - P_1$ is one centimeter,

$$(V_{t2} - V_{t1}) = \frac{1}{1007.4} \cdot 3.5 = .0047 \text{ cm}^3$$

$$V_{g2} - V_{g1} = \frac{1}{2} \cdot 1234 = .0617 \text{ cm}^3$$

$$(V_{b2} - V_{b1}) = (.1183)^2 (3.14) = .0439 \text{ cm}^3$$

When the difference between $P_2 - P_1$ is greater than 1.321 cm (Point B, Figure 2) V_b is calculated by the equation 23. The calculation may be illustrated by the determination of V_b which corresponds to the maximum pressure. The maximum pressure was 1.327 cm therefore $P_2 - P_1$ is 1.327 cm.

$$V_b = .00374 + .05479 = .05853 \text{ cm}^3$$

The values given in Table 16 have been used to plot Figure 6, which is self explanatory.

Let us determine the change in V_c , i.e., the change in the volume of the pressure generator which is necessary to produce a specified pressure change—for example, from 0 to .6 cm. According to equation (20)

$$-V_{c2} = -V_{t2} + V_{g2} + V_{b2} = V_{s2} + V_{b2} \quad (24)$$

To increase the pressure from .6 to .8 cm the additional change

$$-(V_{c3} - V_{c2}) = (V_{s3} - V_{s2}) + (V_{b3} - V_{b2}) \quad (25)$$

is necessary.

Here the subscripts indicate the particular values of the various functions which correspond to point 2 Figure 5.

From equation (25) it follows that

$$\frac{-dp}{dV_c} = \frac{dp}{d(V_b + V_c)}.$$

Obviously, $-\frac{dp}{dV_c}$ is very nearly constant while the upper edge of the meniscus is within the bore. It decreases as the bubble

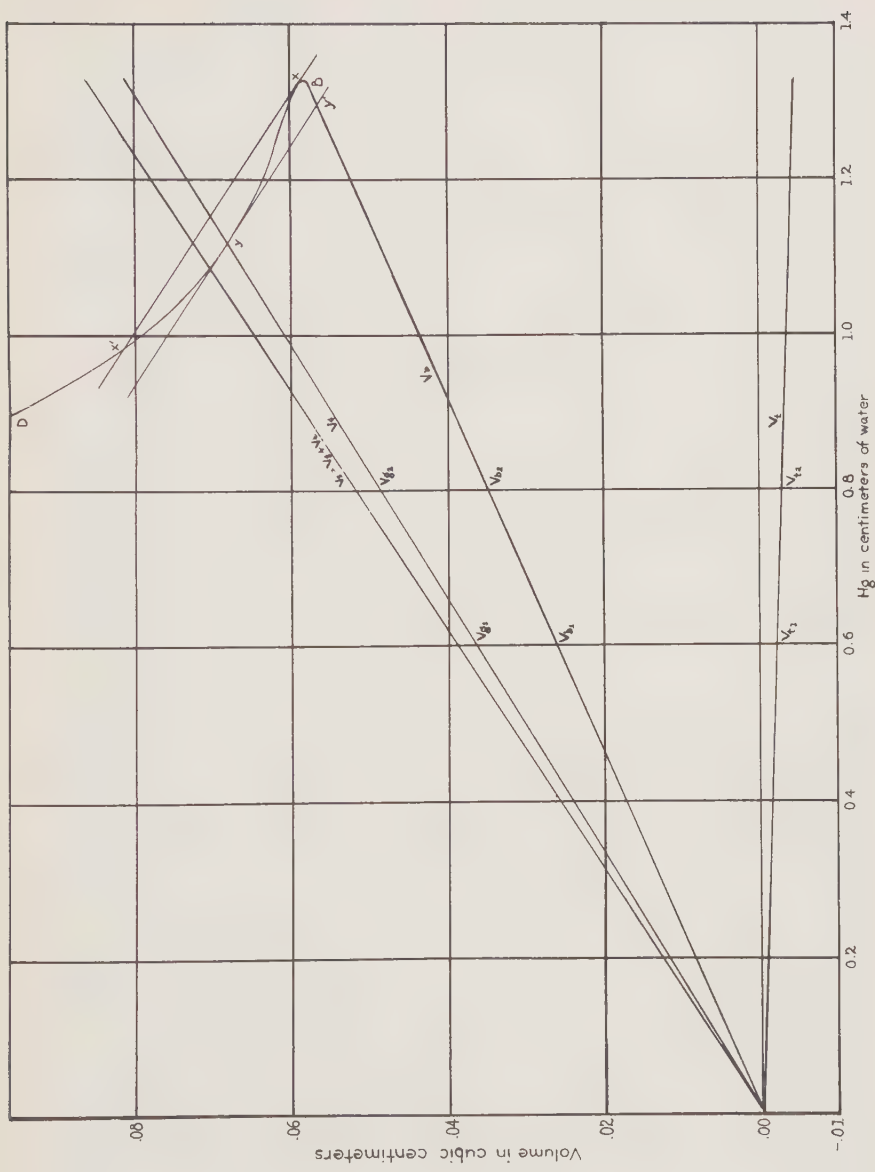


Fig. 6

expands and finally becomes zero when the pressure reaches a maximum and then decreases to negative values. During these periods $\frac{-dV_c}{dP}$ is first positive and nearly constant, and then increases to infinity as the pressure reaches a maximum and then decreases. If the cross-section of the gauge and the volume of the system are large it eventually becomes zero, i.e.,

$$\frac{-dV_c}{dP} = 0 = \frac{dV_b}{dP} + \frac{dV_s}{dP}.$$

This condition is represented by point x on Figure 5.

The value of V_c at the point x is .143 cm³. Since $\frac{dV_s}{dP}$ is zero at this point no point in the neighborhood of x corresponds to a larger value of V_c than .143 cm³. If V_c is changed by an amount ΔV_c the pressure must change to a value such that

$$\Delta V_c + \Delta V_b + \Delta V_s = 0.$$

If the increase in V_c is infinitesimal,

$$\Delta V_b = -\Delta V_s.$$

This condition cannot be satisfied until the point x' is reached. This point may be found by the following procedure. Construct a line with a slope equal to the negative of that of the line V_s and tangent to the curve V_b at x. The point where

$$\Delta V_b = -\Delta V_s$$

is obviously at the intersection of this line with the curve V_b at x'.

As the bubble is further expanded its volume follows the curve V_b . The change in V_c necessary to produce any given pressure may be calculated as previously described. The bubble may be expanded indefinitely or until it is lost from the tip for reasons to be discussed later.

If the diameter of the tip is sufficiently large, $\frac{dV_b}{dP}$

never becomes equal to or less than $\frac{dV_s}{dP}$. Therefore, $-\frac{dV_c}{dP}$ is not at any point equal to or less than zero. Under these conditions the free expansion does not occur and the entire curve may be realized point by point if the pressure generator is compressed slowly. The observations of Frese which were confirmed in this work are in accord with theory. When the cross-section of the gauge and V_t are sufficiently small, it is possible to determine the complete depth pressure curve.

If the diameter of the tip is small (.01 cm), compared to the diameter of the gauge, $-\frac{dV_c}{dP}$ decreases very rapidly to a small value and, consequently, the point of tangency x at which $-\frac{dV_b}{dP}$ becomes equal to $\frac{dV_s}{dP}$ is very near the maximum pressure. Under these conditions the free expansion starts before the pressure decreases appreciably from the maximum.

If the pressure on the generator is relieved, the pressure and volume curve will be retraced in the opposite direction. The volume V_s may be calculated as previously discussed. The value of $-\frac{dV_c}{dP}$ decreases and becomes equal to zero at y . An infinitesimal change in V_c now causes an automatic contraction—that is, a free negative expansion until the pressure recorded by point y' is reached. y' may be determined by a method similar to that used for the determination of x' . A line may be drawn with a slope equal to the negative of curve V_s and tangent to the curve V_b at y . The intersection of this line with V_b is y' . (The points between y and x represent a region which cannot be experimentally realized because the equilibrium between the gauge and the bubble is unstable.)

To confirm this theory an experiment was conducted with the apparatus just described.

The pressure at the time the free expansion started was determined in the following manner. The position of the meniscus in the one arm of the gauge was followed with the cathatometer while the volume of the pressure generator was slowly decreased. The position of the meniscus in the gauge at the inception of the free expansion was recorded for each of three successive bubbles. The corresponding positions of the meniscus in the other arm of the gauge was determined from a second set of three bubbles. Because of the difficulty in determining the point of tangency of a straight line to a curve which is nearly straight, great precision in this determination was not expected; nevertheless, it was possible to show that the free expansion began when the pressure had decreased slightly from the maximum. The pressure was 1.772 cm. At the end of the free expansion from a third series of bubbles, the pressure determined was 1.434 cm. The difference in pressure, .338 cm, is in good agreement with that between x and x' , namely .344 cm. Because of the difficulties encountered in the determination of the point on the curve, and the beginning of the free expansion the agreement is very satisfactory. It is interesting to note that if we apply a correction for the difference between the adiabatic and isothermal expansion, the figure would be replaced by .342. In other words if the system had been allowed to come to temperature equilibrium after the completion of the free expansion the pressure reached would have been .004 cm lower.

We are now in a position to show by an example how curve BD was confirmed, that is, how the values in Table II were obtained. The apparatus used is like the one in the previous experiment. The dimensions are given on page 20.

The pressure in the system after the free expansion was completed, determined in the manner described above was 1.335 cm. The corresponding value of j determined from a third series of bubbles was .361 cm. The maximum pressure measured from another series of bubbles was 1.828 cm.

Effect of Finite Tips: If the inside radius of the tip is sufficiently large the conditions represented by x' may be reached before ϕ' is equal to 180° . If the radius of the tip is smaller x' may be reached when $\phi' = 180^\circ$ and r_c the radius of circular contact has become very large. If the radius is still smaller x' may be reached when r_c is considerably larger than the external radius of the tip. If the external radius of the tip should be smaller than the r_c corresponding to x' the bubble would be lost from the tip before the free expansion is completed. Let us trace the decrease in pressure accompanying the loss of the bubble.

It is necessary to consider in detail the history of the bubble during its growth and loss, especially the volume changes. Let us start with the meniscus at the highest point X_2 (Figure 2) to which it rises in the tube between the escape of two successive bubbles. The meniscus may be forced down by the compressor from X_1 to X_2 where the free expansion starts. The bubble is carried to some point X_3 by the free expansion where it is lost. If the bubble should be severed just at the tip the new meniscus formed at X_4 would retreat into the tube to its original position X_1 since the pressure in the system is not sufficient to retain it at X_4 . As the meniscus rises in the tube, the pressure in the system increases from X_3 to X_1 due to the diminution of the volume.¹

¹The pressure in the system increases slightly from bubble

Let us follow quantitatively the volume changes occurring during the two parts of the cycle. The first will include the reversible expansion; that is, the phenomena accompanying the displacement of the meniscus from x_1 to x_2 .

$$(V_{c2} - V_{c1}) = -(V_{t2} - V_{t1}) + (V_{g2} - V_{g1}) + (V_{b2} - V_{b1}) \quad (25)$$

The second part will include the change during the free expansion; that is, the loss of the bubble, and the subsequent return of the meniscus and the gauge to their original positions.

$$0 = -(V_{t3} - V_{t2}) + (V_{g1} - V_{g2}) + (V_{b1} - V_{b2})$$

The net result of the cycle is the loss of a quantity of gas equal to the volume change of the pressure generator.

$$-(V_{c2} - V_{c1}) = -(V_{t3} - V_{t1}) \quad (26)$$

When the conditions are such that the free expansion starts at the maximum pressure, the pressure changes during the two parts of the cycle are nearly equal, and equation (25) may be used to determine the pressure change if $(V_{t3} - V_{t1})$ is known. Thus we may substitute pressure functions for their volume changes.

$$-(V_{c2} - V_{c1}) - (V_{b2} - V_{b1}) = (P_1 - P_2) \left(-\frac{V_{c0}}{P} + \frac{A'}{Z} \right) \quad (27)$$

When the tube is small, the difference in V_b at the time the upper edge of the meniscus reaches the tip of the tube and at the time the free expansion starts is very small. In the experiments to be discussed later, this difference is approximately .1% of $(V_{b2} - V_{b1})$. The latter quantity is less than .2% of the total

to bubble. Since the volume of the system is decreased when the bubble is lost by an amount equal to the volume of the bubble, the percentage change in the remaining volume, caused by the retreat of the meniscus into the tube is slightly greater than the decrease for the former bubble. For ordinary volumes and small tubes this change in pressure is inappreciable compared to the total change in pressure. The change is approximately one part in a million.

change in the volume ($V_{t3} - V_{t1}$). Under these conditions we may substitute for ($V_{b2} - V_{b1}$) the equivalent pressure function given in equation (22).

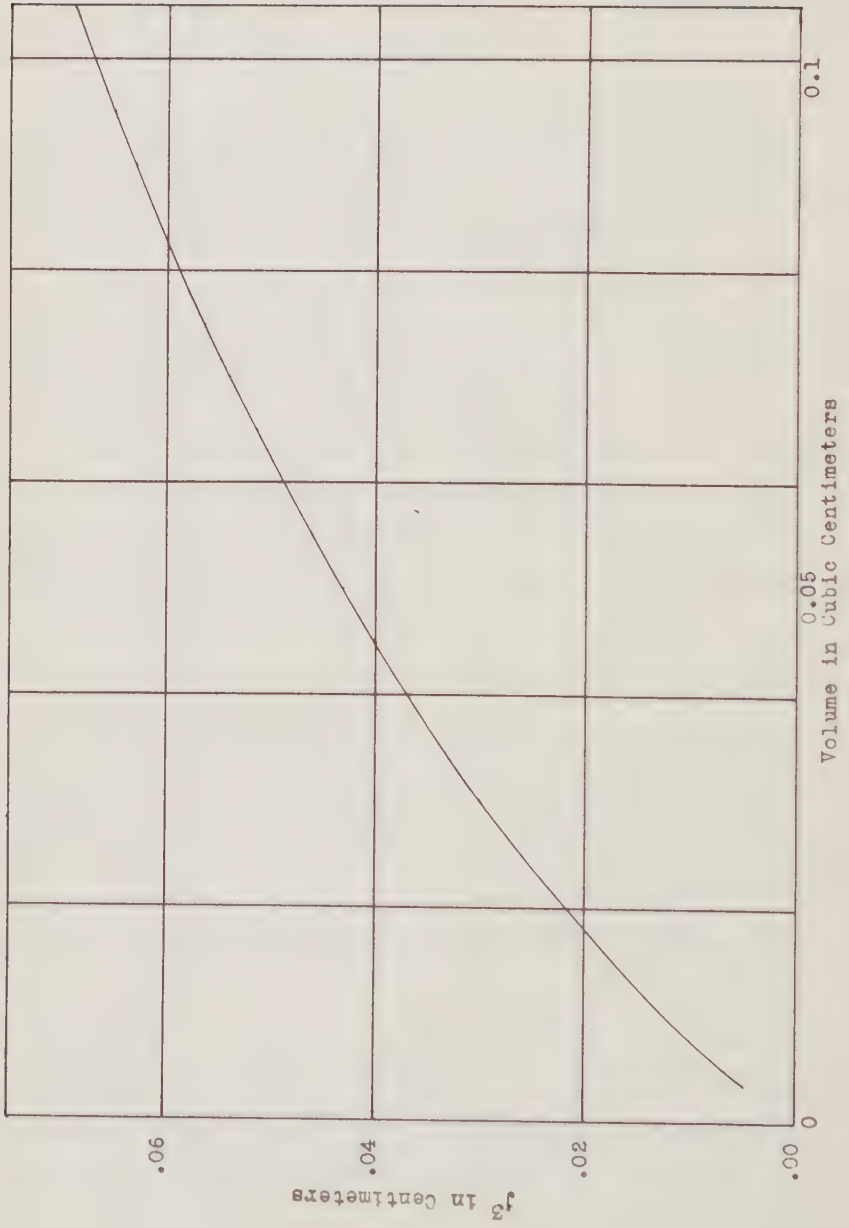
$$-(V_{c2} - V_{c1}) = (P_2 - P_1) \left(-\frac{V_0}{P} + \frac{A'}{Z} + w \right) \quad (28)$$

The volume ($V_{t3} - V_{t2}$) may be computed under certain conditions. Where there is sufficient frictional resistance in the tip the bubble expands slowly and appears to pass through the same series of forms characteristic of an equilibrium expansion. Before it is lost from the tip ϕ' has reached 180° and the diameter of the bubble just before it escapes can be computed from its height and the data in Table 2B. To facilitate the computation, Table 13 has been prepared. Here are presented j , H_g , and r , calculated from Table 2B and the corresponding volumes determined from equation (23a). Since the height of the bubble at the time it is lost may be measured, we may determine its volume approximately, and from this the quantity ($V_{t3} - V_{t1}$). The latter calculation cannot be made exact because the pressure in the escaping bubble is somewhat less than the measured pressure. The error, however, is very small since the pressure in the system has not been as much as 2% above atmospheric pressure in any experiment.

In Figure 7 is given a plot of the volume as a function of the height of the bubble. The ordinate and abscissa represent respectively, the volume, and the cube of the height of the bubble.

This method of calculating the volume of bubbles was tested by comparison with direct experiment. The apparatus used was similar to the one previously used in the measurement of the free expansion. The radius of the gauge was .283 cm. The density of the gauge liquid was .9626. The atmospheric pressure was 1006.4 cm of water. The initial volume of the system V_0 was about

Figure 7



5.0 cm³. The depth of immersion of the tip was approximately one millimeter. The radius of the tip was .0092 cm. The tube was constricted just above the tip to permit about 30 bubbles to escape per minute. At this rate the bubbles were assumed to have their equilibrium shape at the time of escape.

A pressure somewhat in excess of that necessary to liberate bubbles was generated in the system by a large rapid compression of the pressure generator. The excess gas was allowed to escape through the tip until this pressure was dissipated. The number of bubbles discharged while the meniscus moved through 1.164 cm was 84. The pressure remaining in the system after bubbles had ceased to escape was 16.040 cm. The maximum height of the bubbles at the time of their escape measured on another series of bubbles was .176 cm.

The quantity of gas removed from the system because of the decrease in the volume due to the motion of the gauge was

$$(1.164)\pi (.283)^2 = .291 \text{ cm}^3.$$

The quantity of gas which left the system because of the decrease in pressure and its resultant expansion, in accordance with the gas laws was

$$\frac{2(.9655)(1.164)(5.0)}{1006.4 + 16.040} = .011 \text{ cm}^3.$$

The total quantity of gas removed from the system was .303 cm³. The average volume of the bubble was therefore 3.6×10^{-3} cm³. The volume read from Figure 7 for a bubble whose height is .176 cm is likewise 3.6×10^{-3} cm³. Thus there is entire agreement between the calculated and measured values.

To test equation (28) the same apparatus was used. The experimentally determined difference between the maximum pressure and the minimum pressure, i.e., $P_1 - P_2$, was .023 cm. That predicted by the equation (28) was .026 cm.

EFFECTS OF INERTIA AND FRICTION

In our discussion thus far we have dealt with conditions such that the bubble remained on the tip after the free expansion until equilibrium was established, the pressure in the system was increased slowly until the beginning of the free expansion, and the pressure generator was not employed during the free expansion.

When these conditions are changed the behavior of the apparatus may become very complex. For example, conditions may be so adjusted that when bubbles are being formed at the rate of 60 per minute, the fluctuation in the gauge between successive bubbles may be .5% or more of the observed reading. Under other conditions, bubbles may be formed at the same rate on a tip of the same inside radius without producing any noticeable variation in pressure (for example, no pressure variation greater than .01%). If the apparatus is properly constructed this constant pressure may be equal to the theoretical maximum pressure within experimental error; if the design is modified or the rate of bubbling is tripled the observed constant pressure may be 50% too high.

As was earlier anticipated, experiments have shown that the following factors must be considered in a complete study of the apparatus: (1) friction in the tip, (2) rate of flow, and (3) inertia effects.

To study these effects special apparatus was devised. To produce a constant flow of gas a pressure generator was constructed which consisted of a dropping funnel fitted into a 250 cm³ flask. To maintain an unbroken column of the liquid from the

stopcock to the liquid, the end of the delivery tube was drawn out to a fine capillary.

Frictional Effect: For the production of varying frictional effects a stopcock was used. Sealed directly to the barrel of the cock was a piece of capillary tubing of about .05 cm bore. The end of this tubing had been drawn down to form a smaller capillary about one centimeter long terminating in the bubbler tip which had an outside radius of .04 cm, and an inside radius of .013 cm.

The initial volume V_0 was 100 cm³. The specific gravity of the gauge solution was .8092 referred to water at 25°. The depth of immersion of the tip was approximately one millimeter.

The experiment was conducted as follows:

1. With the stopcock wide open, the pressure generator was adjusted so that bubbles were discharged from the tube at the rate of about 16 per minute.

2. The stopcock was turned to impede the flow of gas into the bubbles. The bubbles emerged in groups.

3. The stopcock opening was again slightly decreased until the bubbles formed separately.

4. The opening was again decreased.

The data are presented in Table III. The pressures are in centimeters of the gauge liquid.

The data in Table III show three effects of increasing the resistance in the stopcock.

1. The number of bubbles discharged per minute first increased and then decreased as the resistance was made greater.

2. The height of the bubble and therefore the volume of the bubble decreased to a constant value.

3. The difference between the maximum and minimum pressure decreased.

TABLE III

Frictional Effects Produced by Stopcock

	Number of Bubbles Per Minute	Height of Bubble	Maximum Pressure	Minimum Pressure	Fluctua- tion
Open	16	.242	12.144	12.080	.064
Opening slightly closed . .	Bubbles came in groups				
Opening more reduced .	28	.188	12.144	12.120	.024
Opening again reduced .	Fewer per minute	.188	Pressure rose		

4. When the opening is greatly diminished the pressure mounts to values above the maximum equilibrium pressure.

In the first part of the experiment the frictional resistance was very small. Under these conditions the bubble may be growing very rapidly at the time it starts to leave the tip, but before it is completely severed a large excess volume of gas may flow through the capillary and be lost. The time required for the free expansion and escape of the bubble was estimated to be not more than 2 to 3 per cent of the total time required for the cycle.¹ Consequently, very little gas is supplied by the generator during the latter part of the cycle, and the behavior of the apparatus is similar to that in the previous experiments.

With the introduction of friction into the tube, a pressure in excess of that necessary to displace the meniscus is expected, that is, the maximum pressure recorded by the gauge would be expected to rise above that obtained when there was little

¹Since the free expansion and escape of the bubble requires approximately the same amount of time, regardless of the rate at which the bubbles are being formed, and since the maximum number of bubbles which can be counted in one minute is 300 to 400, the time for expansion must be less than .2 of a second.

frictional resistance in the tube. This effect does not become noticeable, however, until the friction resistance has become very great.

If the stopcock is slightly closed the flow into the bubble is retarded and at the time the bubble is lost its circle of contact is growing slowly. (During the early part of the expansion the bubble grows very rapidly even though considerable friction is applied.) The bubble then starts to escape, for example, by sliding off that edge of the tip which may be higher. During the short interval between the beginning of the detachment and the complete separation from the tip, very little gas enters the bubble. Consequently, the amount of the gas lost is little more than that contained in the bubble when the radius of the circle of contact is equal to the internal radius of the tip. In other words, as the friction is increased, the volume of the bubble approaches one whose circle of contact is equal to the outer circumference of the tip. When this condition is reached the size of the bubble lost becomes independent of the dimensions of the remainder of the apparatus.

Since the fluctuation in pressure is dependent upon the size of the bubble discharged, equation (28) shows that the difference between the maximum and minimum pressure diminished as the friction is increased. Since the rate of flow of gas from the generator has not been changed appreciably during the introduction of the friction and since the quantity of gas escaping in each bubble is less, the number of bubbles per minute increases.

If the friction is again increased, the time required for the radius of contact of the bubble to reach the outside diameter of the tip becomes 50 to 75 per cent of the time required for the whole cycle, and as a result the fluctuation in pressure should

become less. A theoretical basis for this conclusion may be obtained from the following considerations.

As before, equation (25) represents the volume changes during the reversible expansion. The volume changes occurring during the second part of the cycle are

$$-(V_{c3} - V_{c2}) = -(V_{t3} - V_{t2}) + (V_{g1} - V_{g2}) + (V_{b1} - V_{b2}) \quad (29)$$

For the cycle then,

$$-(V_{c3} - V_{c2}) + -(V_{c2} - V_{c1}) = -(V_{t3} - V_{t1}).$$

Combining with (25) and rearranging we obtain

$$-(V_{t3} - V_{t2}) + -(V_{c2} - V_{c1}) = (P_2 - P_1) \left(-\frac{V_0}{P_1} + \frac{A^1}{2} + w \right) \quad (30)$$

As the friction is increased the bubble expands more slowly and is retained on the tip for a longer period of time. Under these conditions the free expansion required a longer time during which the compressor continued to operate and as a result $(V_{c2} - V_{c1})$ increases. As $(V_{c3} - V_{c2})$ approaches $(V_{t3} - V_{t1})$ the pressure $(P_2 - P_1)$ approaches zero. Therefore, as the friction is increased the fluctuation in pressure decreases.

Before discussing the observation that the maximum pressure within certain limits is independent of the frictional resistance in the tube let us describe another experiment in which the friction was increased markedly by an increase in the rate of flow from the pressure generator.

Effect of Changing the Rate of Flow from the Generator:

The apparatus was the same as that used to determine the frictional effects, except that the stopcock tube was replaced by one which had been constricted above the tip to insure a slow expansion of the bubble. The radius of the tip was .0092 cm. The specific gravity of the gauge liquid referred to water at 25° was .9655. The following observations were made when gas was forced

into the apparatus at varying rates. The pressures are in centimeters of the gauge solution.

TABLE IV
Effect Produced by Changing the Rate of Flow

Bubbles per Minute	Maximum Pressure	Minimum Pressure	Fluctuation
5	16.020	15.990	.030
7	16.016	15.988	.032
15	16.016	15.993	.023
30	16.018	16.018	.000
40	16.018	16.018	.000
50	16.014	16.014	.000
74	16.018	16.018	.000
Gauge fluctuating; no readings possible	. . .	. . .	
140	16.004	16.004	.000
Pressure mounts to higher values			

Table IV shows four effects due to increased rate of flow.

1. At slow bubbling rates a fluctuation in pressure was observed as each bubble was discharged. The maximum values were the same as the theoretical, i.e., those determined from infinitely slow rates of bubbling.

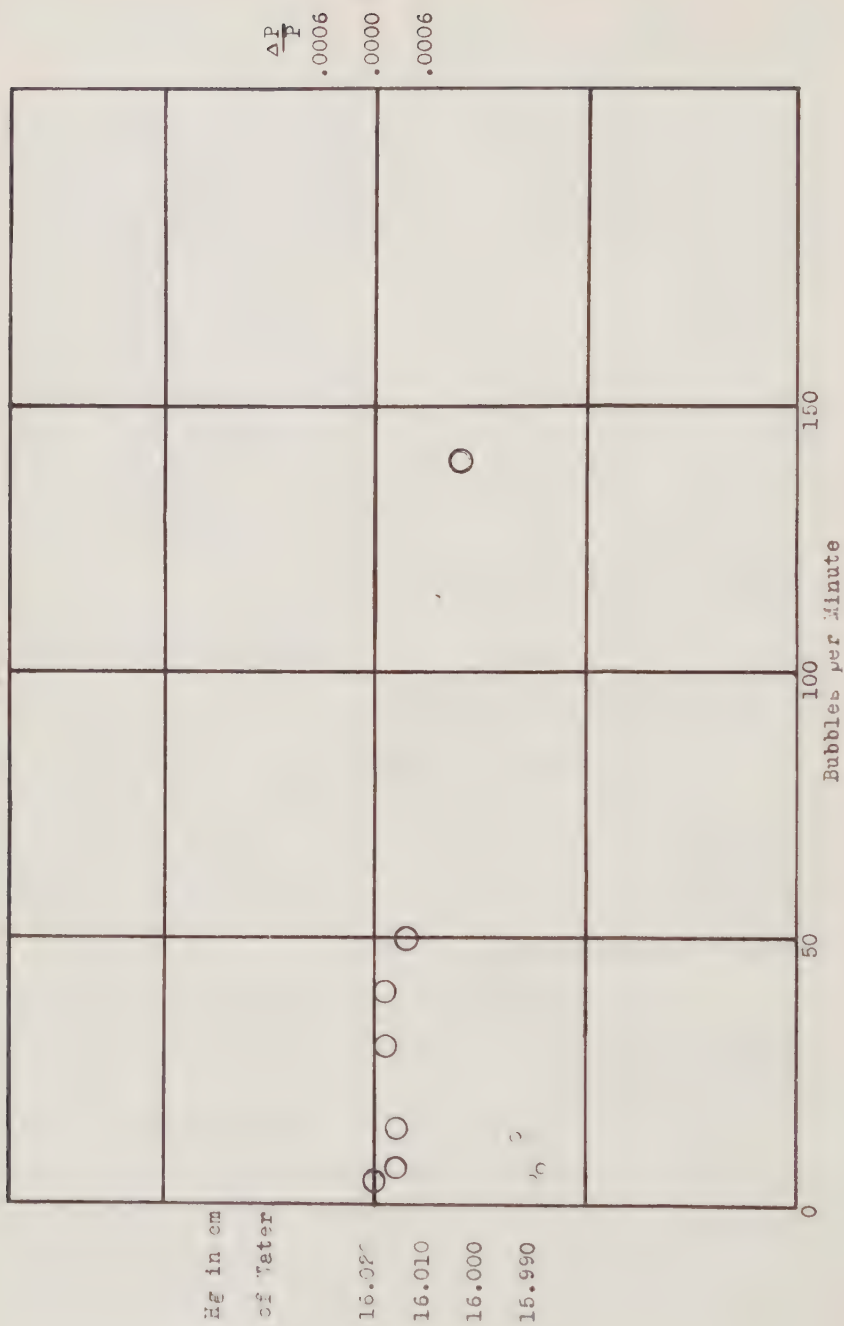
2. From approximately 30 to 75 bubbles per minute the pressure was essentially constant. At faster rates of bubbling the gauge oscillated.

3. A minimum in the pressure curve was obtained when bubbles appeared at the rate of 140 per minute.

4. When bubbles were discharged at a very rapid rate, the pressure increased to values higher than the original theoretical.

The data given in Table IV are plotted in Figure 8. The

Figure 8



ordinate which represents the pressure is marked on the left hand margin in centimeters of the liquid. On the right margin the figures designate the ratio of the change in pressure to the total applied pressure. The abscissa represents the number of bubbles discharged per minute. The line marked 16.020 depicts the maximum pressure attained in bubbles that were formed very slowly. The small circles designate the minimum pressure due to the fluctuation.

When the rate of flow is very slow, the quantity of gas supplied by the generator during the latter part of the cycle is very small in comparison to that supplied during the complete cycle. If the rate of flow is increased, the quantity of gas required to liberate a bubble is passed into the system in a much shorter period of time and as a result the time required for the cycle is shortened. However, the time required for the free expansion does not change with the rate of flow since the pressure in the system does not change more than 2% during the loss of a bubble. Since the rate of flow from the generator does not change throughout the cycle, the quantity of gas supplied by the generator is now an important part of the gas entering the bubble. In other words the term $(V_{c3} - V_{c2})$ in equation (29) becomes larger as the rate of flow is increased. As we have pointed out, when $(V_{c3} - V_{c2})$ approaches $(V_{c2} - V_{c3})$, the difference between the maximum and minimum pressure disappears.

We may now discuss the phenomenon that the maximum pressure is within certain limits not affected by an increase in friction. Before it is possible to investigate this phenomenon, it is necessary to develop a method for the calculation and determination of the pressure required to force a given volume of gas through the tube. That sufficient gas is flowing through the tube

to cause an excess pressure is shown by the following experiment. A tube was sealed on the bottom of the apparatus that was used to study the varying frictional effects so that the level of the liquid might be lowered below the level of the tip.

The tube was fastened firmly in place. The flow of the mercury was adjusted so that bubbles would escape at the rate of 30 per minute. The level of the liquid in the well was then lowered below the tip. The pressure in the system fell gradually to .130 and remained constant within .01 cm. The level of the water was then restored. The pressure returned to approximately its original value. The process was repeated at different rates. The height of the bubble was .243 cm. The data for a series of tests are presented in Table V. The first column gives the number of bubbles discharged per minute, the second column gives the pressure remaining in the system after the gauge had come to equilibrium. The third column gives the pressure predicted by the Poiseuille Equation. The pressures are given in centimeters of water.

TABLE V
Experimental and Theoretical Pressures Required to
Force Gas through a Capillary Tube

Number of Bubbles per Minute	Pressure Remaining in the System (Experimental)	Pressure Predicted by Poiseuille Equation
17	.100	.068
25	.110	.100
30	.130	.120
60	.240	.240
92	.370	.368
120	.466	.480

The pressure H required to force the gas through the capillary was determined from the Poiseuille equation

$$H = \frac{8\eta CV}{\pi r^4 T}$$

where η is the coefficient of viscosity of the air, C the length of the constriction in the tube, and t the time in seconds. Let us calculate the pressure necessary to force 30 bubbles per minute through the tip used in the experiment. $\eta = 1.84 \times 10^{-4}$, C = 1.1 cm, V = .0115 cm³, and T = 2 seconds.

$$H = \frac{(8) (.000184) (1.1) (.0114)}{(\pi) (.0135)^4 (2) (3.14)}$$

$$H = .120 \text{ cm.}$$

This effect is about 1% of the pressure necessary to liberate bubbles yet no error results in the measurement of the maximum pressure. A simple theory in accord with all the known facts has been developed to explain this observation.

When the liquid is below the tip the difference in pressure between the ends of the constriction is constant, and the flow of gas through the tube is constant. When the level of the liquid is above the tip the gas flow through the tube is irregular and it is only during the free expansion that gas flows through the tube at a high rate of speed. During the reversible expansion the only volume change in the tube is that due to the depression of the meniscus. This volume may be determined from equation (23) if the pressure change is known. Let us calculate the pressure H necessary to force this volume of gas through the tube when bubbles are emerging at the rate of 28 per minute and the fluctuation in pressure is .019 cm. The time required for the free expansion is approximately 1.9 seconds. The volume is

$$(V_{b2} - V_{b1}) = .019 \times (.135)^2 \times 3.14 = 1.1 \times 10^{-5} \text{ cm}^3$$

At the maximum the excess pressure is then

$$H = \frac{(8) (.000184) (1.1) (.000011)}{(.8019) (980.1) (.0135)^4 (1.9) (3.14)}$$

$$H = 1.1 \times 10^{-4} \text{ cm.}$$

The rush of gas through the tube in the subsequent period does not affect the maximum pressure.

For these conditions a volume of water equal to the volume of gas namely, $1.1 \times 10^{-5} \text{ cm}^3$ was displaced from the tube. As before we may use the Poiseuille Equation to determine the pressure H necessary to overcome the frictional forces. C in this case, is equal to .019/2 cm, one-half the distance the meniscus rises in the tube between two successive bubbles, that is, from X_2 to X_1 . The excess pressure is

$$H = 5. \times 10^{-5} \text{ cm.}$$

Since it is only during the reversible expansion that frictional forces can affect the maximum pressure attained in the particular bubble we are concerned with the subsequent expansion of the bubble only in so far as it may affect the pressure attained in the following bubble.

We may conclude from the calculations that within limits the maximum pressure is independent of the frictional resistance.

Influence of Inertia: The oscillation and the minimum observed in the constant pressure when bubbles were discharged at the rate of 75 to 140 per minute may be due to inertia effects. We have not investigated all the factors contributing to the phenomena represented by this portion of the curve. Indeed, the very presence of these phenomena make it impossible to obtain surface tension data from measurements of the maximum pressure in bubbles under these conditions.

It seems likely that the oscillation is due to some

resonance or beat effects approaching the natural period of oscillation of some portion or portions of the apparatus such as the gauge, for example.

When bubbles are discharged rapidly they seem to form a chain, such that one bubble can hardly be distinguished from another. Under these conditions, the bubble formed may not assume the equilibrium shape and as a result the pressure inside is not equal to that inside a bubble which is expanding under equilibrium conditions. The pressures formed in this manner may be due to a combination of surface tension and frictional forces.

The influence of friction on this minimum found in the constant pressure is shown by the following experiment. The apparatus was similar to the one used to determine the frictional effects. With the stopcock wide open bubbles were formed slowly and the maximum pressure recorded. The rate of bubbling was increased to approximately 140 per minute. The pressure indicated was noted. The opening of the stopcock was slightly decreased and the measurements repeated. For three successive openings of the stopcock, the differences between the maximum pressure obtained when bubbles were discharged slowly, and that at higher rates of speed were: .072, .035, and .020 cm.

The results of the experiment on the rate of bubbling may now be summarized: The data show that when bubbles are discharged at a rate of less than 30 per minute, an oscillation in the gauge occurs as each bubble is discharged. The maximum pressure under these conditions is found to be equal to that in bubbles formed slowly and allowed to remain at the maximum pressure for a period of time.

An increase in the rate of flow does not change the maximum pressure but the fluctuation in pressure accompanying the loss

of the bubble vanishes. This essentially constant pressure is equal to the maximum pressure until the rate of bubbles discharged per minute has been increased to 80. Here the gauge begins to oscillate presumably because of resonance and beat effects. When the rate of flow is increased to 140 bubbles per minute, a constant pressure slightly lower than the original maximum is observed. A further increase in the rate of flow causes a pressure in excess of the true maximum.

It has been shown that for the essentially constant pressure observed when bubbles are discharged at the rate of 30 to 75 per minute the fluctuation in pressure vanishes. Calculations with the Poiseuille Equation indicate that noticeable frictional forces are not present. Inertia effects, which are significant at higher rates of flow do not appear.

APPLICATIONS TO SURFACE TENSION MEASUREMENTS

As a result of these findings it becomes evident that there are certain characteristics which must be incorporated in the design of apparatus which will liberate bubbles rapidly at just that pressure equal to the maximum pressure attained in the very slow formation of bubbles: (1) the outside diameter of the tip must not be too large; (2) the frictional resistance offered by the tube must be properly adjusted; (3) the diameter of the gauge and the volume of the system must not be too small.

(1) If the outside diameter of the tip is large, the bubble is retained until it is very large. If there is little friction in the tip, the pressure decrease is very large. A constant pressure obtained under these conditions is likely to be a combination of inertia and surface tension forces. If sufficient friction is present to insure slow growth of the bubble, a constant pressure may result as an improbable combination of surface tension and frictional forces.

(2) If the frictional resistance in the tip is too high, a pressure in excess of that necessary to overcome the surface tension forces will be required to liberate bubbles. This situation is easily detected, since the maximum pressure varies with the rate of flow. If the frictional resistance is not sufficient, the bubbles are not liberated singly, but in groups of two or more. Under these conditions, the gauge may oscillate through several tenths of a millimeter or more. The connecting tube between the gauge and the tip should be free from constrictions,

because frictional forces occurring under these conditions are additive and cause an excess pressure to be recorded by the gauge.

(3) When the diameter of the gauge or the volume of the system is too small, the decrease in pressure accompanying the loss of the bubble is very large. This results in more gauge oscillation and because of inertia effects the pressure may not reach the true maximum.

Sugden's Method: It is now possible to examine Sugden's method with the aid of the conclusions hitherto reached. His apparatus consisted of two tips of different sizes. The bubbles are formed slowly on the larger tip, but very rapidly on the smaller one; the latter consisted of a small capillary tube made from thin walled tubing. The apparatus was so constructed that he observed little oscillation in the pressure when bubbles were passing through at the rate of one per second. For his surface tension measurements Sugden used the constant pressure that is observed when bubbles are formed at the rate of 40 to 75 bubbles per minute. He computed the surface tension of water and benzene from the observed pressure and the radius of the tips, and found them to be in very good agreement with values obtained by other methods. He did not, however, show directly that his observed pressure attained in the liberation of the bubbles from the small tube was precisely equal to the maximum pressure obtained when bubbles were formed slowly. Nor does he mention the very high and erroneous results obtained in the more rapid bubbling. He uses the thin walled tips which have been shown to be necessary, but he does not mention any experiments with heavy walled tips. Had these been used, correct results could not have been obtained.

Sugden and Schrodinger have pointed out large errors formerly existing in the maximum bubble pressure method. The

possible errors still existing in the Sugden method are probably less fundamental than the errors which have been corrected; it is even possible that by accidental cancellation of the various errors that some if not all of Sugden's measurements are approximately correct. On the other hand, there appears to be no systematic arrangement for cancellation of these errors. He apparently knew no more about the effect of friction or of the volume of his system than of the importance of thin walled tubes. It is highly probable that one using a similar apparatus would introduce very large errors if he were not informed of the difficulties involved.

Since there is no advantage to be gained by rapid bubbling it seems best to avoid all these uncertainties by the very slow formation of bubbles. In such a procedure frictional, inertia, and volume effects lose their significance.

SUMMARY

It has been shown in this laboratory that large errors have been introduced by improper theory and less important technique into the capillary rise, the drop weight, and the maximum-pull-on-a-ring method of measuring surface tension. Because of these mistakes, errors as large as 3% in the capillary rise and 40% in the drop weight and the ring method have occurred. An investigation of the maximum bubble pressure method has now been made.

The history of the meniscus has been traced during its displacement from the normal position (that of capillary rise) to the end of the tube, during the change of ϕ' from 90° to 180° , and during the further expansion as its depth passes through a maximum and finally approaches a constant value. Curves have been constructed which depict the height of the bubble as a function of the difference in pressure between the free surface of the liquid and the vertex; as a function of the pressure between the inside and outside of the bubble at the vertex; and as a function of the total pressure, i.e., the difference in pressure measured by a manometer connected to the capillary tube. Curves which show the variation of the height of a bubble as a function of this pressure for a series of values of the parameter r/a have been constructed. Experimental verification of the height pressure curve has been extended into the region of the curve where $\phi' = 180^\circ$.

A qualitative and quantitative explanation of the free

expansion has been given in terms of the constants of the system, which are: (1) the value of r/a , (2) the radius of the gauge, (3) the volume of the system, and (4) the outside diameter of the tip. Formulas by which the magnitude of the free expansion may be predicted have been developed.

Investigation of the frictional effects produced by the variation of the dimensions of the tube have shown that the friction affects the fluctuation in pressure between bubbles, but that within certain limits does not affect the maximum pressure. An investigation of the behavior of the apparatus when the rate of flow is increasing showed that the fluctuation in pressure vanishes. It was found that at certain rates of flow, the pressure recorded by the gauge is essentially constant and equal to the maximum pressure observed when bubbles are formed slowly. At higher rates of flow inertia and frictional effects become important.

It was found that if bubbles are to be liberated rapidly from a small tip at just that pressure necessary to liberate bubbles at the equilibrium pressure, the tips must have thin walls, the volume of the system and the radius of the gauge must be large, and the friction must be properly adjusted, although considerable latitude can be tolerated.

Sugden's apparatus probably met most of these conditions, but he did not give and apparently did not have any good reasons for adopting the particular dimensions of his apparatus.

Rapid bubbling is not recommended for surface tension measurements, since it is possible to avoid the uncertainties of friction and inertia if the bubble is formed slowly.

A P P E N D I X E S

APPENDIX A

TABULAR MATERIAL

TABLE 1

(Employed to construct curves OB'F' and OBF, Fig. 2)

Values of P_0/a , H_g/a , and j/a

(Used to construct curve OD' and OD) $r/a = .3386^*$

	ϕ'	x/b	z/b	P_0/a	j/a	H_g/a
8.0000 . .	10.03	.1692	.0156	.531	.0313	.5625
2.0000 . .	20.42	.3386	.0603	1.000	.0602	1.0602
1.0000 . .	29.57	.4788	.1246	1.412	.0081	1.5021
.8000 . .	33.50	.5353	.1594	1.618	.1008	2.2029
.2500 . .	69.91	.8741	.6324	2.5819	.2449	2.8269
.2500 . .	84.00			2.8222	.3190	3.1212
.2470 . .	90.00	.96341	.9174	2.8452	.3203	3.1678
.2500 . .	96.42	.9577	.9914	2.8290	.3503	3.1792
.2537 . .	100.00	.9504	1.0601	2.8071	.3776	3.1847
.2621 . .	105.00	.9352	1.1288	2.7620	.4086	3.1700
.3143 . .	120.00	.85399	1.2828	2.5175	.5086	3.0287
.5000 . .	144.23	.6771	1.38431	1.9997	.5922	2.5920
.7500 . .	163.23	.5527	1.3396	1.6328	.8200	2.4523
1.0786 . .	180.00	.4699	1.2526	1.3878	.9026	2.2073

*These values with the exception of those for $\phi' = 180^\circ$ were taken from Hoffman's thesis. They were originally in the dimension of the square root of the capillary constant of water.

TABLE 2

(Employed to construct curves OB'F' and OBF, Fig. 2)

Values of P_0/a , H_g/a , and j/a

(Used to construct curve D' Ω ' and D Ω) $\rho' = 180^\circ$

	r/a	x/b	z/b	P_0/a	H_g/a	j/a
.1250 . .	.0646	.2586	1.7848	4.0000	4.4462	.4462
.2500 . .	.1182	.3344	1.6537	2.8031	3.4144	.5847
.5000 . .	.2047	.4094	1.4769	2.0000	2.739	.7384
.7500 . .	.2737	.4469	1.3558	1.6630	2.462	.8303
.8965 . .	.3081	.4602	1.3006	1.4932	2.3639	.8708
1.0000 . .	.3313	.4685	1.2646	1.4142	2.3084	.8942
1.0786 . .	.3386	.4699	1.2526	1.3878	2.2073	.9026
1.3686 . .	.4021	.4861	1.1633	1.2054	2.1709	.9622
1.5000 . .	.4246	.4903	1.1322	1.1549	2.1354	.9805
2.0000 . .	.4989	.4989	1.0381	1.0000	2.0382	1.0382
8.0000 . .	.9313	.4656	1.2592	.5000	1.7520	1.2592
18.0000 . .	1.2218	.4073	1.3445	.3333	1.6779	1.3444
32.0000 . .	1.4368	.3692	1.3883	.2500	1.6332	1.3884
50.0000 . .	1.7066	.3213	1.4145	.2000	1.6145	1.4145
72.0000 . .	1.7464	.2911	1.4319	.1666	1.5989	1.4319
98.0000 . .	1.8652	.2665	1.4439	.1428	1.5868	1.4440

TABLE 3

(Employed to construct curves OB'F' and OBF, Fig. 2)

Values of P_0/a , H_g/a , and j/a

(Used to construct curve Ω 'F' and Ω -F) $\rho' = 180^\circ$

L	P_0/a	H_g/a	j/a
3	.0486	1.526	1.477
4	.0137	1.496	1.485
5	.0039	1.481	1.477
6	.0010	1.469	1.469

TABLE 4*

(Employed in the drawing of meniscus and bubble forms of Fig. 3)

Values of x , z , and the parameter ϕ for $r/a = .3385$

Part A (used for drawing curve 2) $\beta = 1$

ϕ	x	z
5°	.061564	.0026823
10	.12231	.010677
15	.1815	.023803
20	.23836	.041720
25	.29235	.23595
29.57	.33855	.88102

*Tables 4A - 4D, inclusive, were taken from Hoffman's Thesis. They were originally in the dimensions of the square root of the capillary constant of water.

Part B (used for drawing curve 3) $\beta = .3$

ϕ	x	z
15°	.1000	.0132
30	.1918	.0511
45	.2685	.1099
60	.3252	.1836
69.91	.3386	.2449

Part C (used for drawing curve b) $\beta = .75$

ϕ	x	z
5°	.0306	.0013
15	.0907	.0119
30	.1743	.0465
45	.2444	.1002

Part C (Continued)

ϕ	x	z
60°	.2966	.1681
75	.3281	.2442
90	.3386	.3224

Part D (used for drawing curve c) $\beta = .25370$

ϕ	x	z
5	.0310	.0014
15	.0919	.0121
30	.1767	.0471
45	.2477	.1016
60	.3005	.1703
75	.3325	.2473
90	.3430	.3264
100	.3386	.3776

Part E (used for drawing curve d) $\beta = 1.0786$

ϕ	x	z
15°	.1848	.02422
30	.3490	.09193
45	.4787	.1910
60	.5769	.3077
75	.6198	.4303
90	.6355	.5480
105	.62184	.6571
120	.5840	.7464

Part E (Continued)

ϕ	x	z
135°	.5301	.8174
150	.4664	.8663
165	.406207	.8992
180	.3386	.9026

Part F (used for drawing curve λ) $\beta = 2$

ϕ	x	z
15	.2546	.0332
30	.4720	.01226
45	.6347	.2466
60	.7420	.3855
75	.8005	.5255
90	.8182	.6572
105	.8031	.7740
120	.7630	.8716
135	.7053	.9472
150	.6374	.9995
165	.5665	1.0291
180	.4989	1.0381

TABLE 5

Values of H_g/a , j/a , and assigned values of the Parameter ρ'

for $r/a = .3031$

(Employed to construct curve $A_1B_1D_1$, Figure 5)

ρ		H_g/a	j/a	x/b	z/b
90	.2019	3.442	.2956	.9695	.9305
95	.2036	3.455	.3204	.9559	1.0048
100	.2077	3.452	.3469	.9558	1.0764
105	.2150	3.423	.3752	.9392	1.1439
110	.2258	3.381	.4057	.9668	1.2074
115	.2400	3.321	.4360	.8891	1.2584
120	.2584	3.253	.4719	.8569	1.3126
135	.3425	2.998	.5831	.7444	1.4092
150	.4778	2.742	.6970	.6300	1.4255
165	.6690	2.527	.7987	.5326	1.3813
175	.8179	2.413	.8514	.4817	1.3291
180	.8965	2.363	.8707	.4601	1.3006

TABLE 6

Values of H_g/a , j/a , and assigned values of the Parameter ρ'

for $r/a = .4021$

(Employed to construct curves $A_3B_3D_3$, Figure 5)

ρ'	H_g/a	j/a
90	2.7365	.3761
95	2.7584	.4060
100	2.7598	.4378
102.72	2.7662	.4570
104.56	2.7620	.4682

TABLE 6 (Continued)

ρ'	H_g/a	j/a
115.00	2.7175	.5417
126.87	2.6292	.6289
148.05	2.4256	.7914
175.00	2.2047	.9430
180.00	2.1709	.9622

TABLE 7

Values of H_g/a , j/a , and ρ' for $r/a = 1$
(Employed to construct curve A4B4D4, Figure 5)

ρ	H_g/a	j/a
90	1.4950	.7508
147.1	1.7480	1.1704
152.6	1.7520	1.1972
157.5	1.7537	1.2185
162.1	1.7526	1.2360
166.0	1.7513	1.2508

TABLE 8

Values of H_g/a , j/a , and the parameter r/a for $\rho' = 90^\circ$
(Employed to construct curve B, Figure 5)

r/a	H_g/a	z/a
.2451	4.238	.238
.3081	3.4421	.2956
.3386	3.1678	.3203
.3401	3.1541	.3240

TABLE 8 (Continued)

r/a	H_g/a	z/a
.4021	2.7366	.3761
.4664	2.4275	.4275
.5555	2.1268	.4938
.8182	1.6571	.6572
1.0000	1.4950	.7508
1.2789	1.3495	.8495
1.5778	1.2617	.9283
1.7967	1.2199	.9699
1.9686	1.1952	.9952
2.1099	1.1785	1.0119
2.2297	1.1664	1.0236

TABLE 9

Values of H_g/a , j/a , and the parameter r/a when $\rho' = 90^\circ$
 (Employed in the construction of curve B, Fig. 5)

	H_g/a	j/a
3	1.136	1.088
4	1.115	1.091
5	1.085	1.081
6	1.059	1.058

TABLE 10

Maximum values of H_g/a and the corresponding values
of j/a and r/a
(Employed in the construction of Curve C, Fig. 5)

r/a	H_g/a	j/a
.3081	3.4553	.3204
.3385	3.1847	.3776
.4021	2.7662	.4570
1.0000	1.7537	1.2185

TABLE 11

Values of the Functions (employed to construct curves V_b ,
 V_t , V_g , and V_s , Fig. 6)

H_g	$V_b \text{ cm}^3$	V_t	V_g	V_s
.1000	.00440	.00034	.0061	.0065
.2000	.00878	.00064	.0123	.0130
.4000	.01756	.00139	.0246	.0260
.6000	.02634	.00206	.0368	.0389
.8000	.03515	.00279	.0494	.0522
1.0000	.04396	.00347	.0617	.0652
1.3217	.05803	.00457	.0814	.0861
1.3268	.05853	.00462	.0815	.0862

TABLE 12

Values of H_g , V_b , and assigned values of the parameter
for $r = .3081$ cm, and $a = .38399$ cm
(Employed to construct curve CD, Figure 6)

ϕ'	H_g	V/b^3	V_b
95°	1.3268	2.0418	.05853
100	1.3243	2.8152	.05893
105	1.3146	2.4384	.05964
110	1.2983	2.6023	.06037
115	1.2755	2.7284	.06120
120	1.2491	2.8393	.06199
135	1.1515	2.9703	.06660
150	1.0530	2.8452	.07361
165	.9705	2.6246	.08264
175	.9266	2.4535	.09112
180	.9077	2.3526	.09494

TABLE 13

Values of j and V_b (proper) and assigned values of the
parameter r/a for $\phi' = 180^\circ$
(Employed to construct Figure 7)

	r_c	H_g	j	V_b
.125	.02482	1.7075	.1707	.0033
.250	.04539	1.3105	.2245	.0084
.500	.07860	1.0504	.2838	.0204
.750	.10508	.9485	.3160	.0328
1.000	.12722	.8863	.3433	.0451
1.500	.16308	.8200	.3766	.0684

TABLE 13 (Continued)

	r_c	H_g	j	V_b
2.000	.19155	.7825	.3987	.0902
8.000	.37760	.6756	.4835	.2713
18.000	.46918	.6443	.5162	
32.000	.55173	.6291	.5331	.6010
50.000	.61689	.6199	.5432	
72.000	.67061	.6138	.5498	.8672
98.000	.71622	.6093	.5545	.9861

APPENDIX B

NOTATIONS

a = square root of the capillary constant

b = radius of curvature at the vertex of the meniscus or bubble

$$\beta = g(D - d)zb^2 = \frac{2b^2}{a}$$

C = length of constriction in the tube

D = density of liquid

d = density of light phase

g = acceleration of gravity

H_g = sustaining pressure

$$h = \frac{\bar{p}}{(D - d)g}$$

j = the height of the vertex of the bubble above the tip of the tube

L = maximum diameter of a large bubble

p = pressure difference at varying depths on the two sides of a bubble

$\bar{p}$ = maximum pressure difference inside and outside the bubble at the level of the end of the tip

P_0 = pressure difference between two sides of any bubble or meniscus at the vertex

P = sum of applied pressure and atmospheric pressure in centimeters of the liquid

r = radius of the tip

r_0 = circle of contact of the bubble with the horizontal

edge of the tip

s = density of liquid used in the gauge

t = depth of immersion of the tip below free surface of the liquid

V_b = increment of volume produced by the depression of the meniscus in the capillary tube

V_c = increment of volume produced by the contraction of the generator

V_t = change in the total volume

V_o = volume of the system when the applied pressure is zero

V_s = sum of V_g and V_t

V_t = change in the total volume of the system

w = cross-section of the capillary tip

x = horizontal coordinate referred to the vertex of the bubble as the origin

z = vertical coordinate referred to vertex of the bubble as origin

A = cross-section of the gauge

$$A' = \frac{D}{d}$$

γ = surface tension in dynes centimeters

R' and R = principal radii of curvature in the La Place equation

= radius of curvature

ϕ and ϕ' = angles lying between the vertical axis and the normal to the surface of the bubble

